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# sthyl bromide alternatives

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# Update on Field Tests for Preplant Methyl Bromide Alternatives

As mentioned in this newsletter's January issue, Congress appropriated an increase of \$750,000 in FY 1996 to the Agricultural Research Service for methyl bromide work. Of that amount, \$550,000 is being used to establish projects in California and Florida for large-scale field tests of potential alternatives to methyl bromide. Work is well under way in both States.

Tom Trout (ARS-Fresno, California) reports that plans are progressing in California for field-testing cropping practices that have the best chance of success with strawberry and perennial crops without use of methyl bromide. Teams of ARS and University of California scientists are selecting practices to incorporate into viable cropping systems.

Because growing strawberries is very specialized, the California Strawberry Commission is serving as liaison between the project and commercial growers to arrange for land and production practices to be used in the field studies. Production practices on the plots will closely duplicate those used on growers' fields. A cooperative agreement with the commission will help cover the high production costs. ARS and UC scientists, and the commission, will

cooperatively select practices and set up and monitor the demonstration sites, located in the central and southern coastal areas of the State. Practices on strawberries will include alternative forms of preplant soil fumigation; improved management of soil, water, and nutrients; and some exploration of biological control measures. Strawberry demonstration plots will be planted this fall.

For perennial crops, representatives of 12 grower groups—including fruit, nut, and vineyard growers—met with scientists in Fresno in January to help scope out and prioritize needs and alternatives. This group will meet annually to review plans and results.

ARS recently purchased a research farm in a prime orchard and grapegrowing area near Parlier, California. Scientists will take out and replant peach orchards and vineyards on the farm over the next 2 years to study the replant problem. Project funds will be used to cover production costs of the field trials carried out cooperatively by ARS and UC scientists. In addition, research costs of field trials conducted by Mike McKenry and Becky Westerdahl, UC nematologists, are being covered by cooperative agreements. Cropping practices to be demonstrated will include ways to kill roots of the removed crop, fallowing before replanting, fumigating with alternative chemicals, and managing water and nutrients to maximize vigor of the young plants.

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This newsletter provides information on research for methyl bromide alternatives from USDA, universities, and industry.

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On the field tests in Florida, ARS is cooperating with the Florida Fruit and Vegetable Research and Education Foundation and the University of Florida's Institute of Food and Agricultural Sciences, according to ARS's David Patterson at Fort Pierce. Field-scale validation of methyl bromide alternatives for tomato production will begin with the fall 1996 planting season.

Five locations have been chosen: North Florida (Quincy), West Central Florida (Ruskin/Palmetto), Southwest Florida (Immokalee), Southeast Florida (Palm Beach County), and South Florida (Homestead). Grower cooperators are currently being identified for these areas.

The primary methyl bromide alternative to be tested is Telone C-17 at 35gal/acre with Tillam herbicide at 4 lb/acre. Solarization treatments continue to be evaluated at Quincy.

# Carbonyl Sulfide: Possible Alternative Fumigant To Replace Methyl Bromide

U.S. growers produce more than \$1.5 billion worth of dried fruits and nuts each year. Not only do consumers in the United States and abroad love these commodities, but so do a wide range of insect pests. Currently, 100 percent of stored dried fruits and nuts are treated with methyl bromide or phosphine to rid them of these pests.

Methyl bromide is scheduled for elimination in 2001, and phosphine is also under attack because of human health concerns and pest resistance. There is no viable replacement for either fumigant.

"But we've found a possibility," says ARS entomologist J. Larry Zettler. At the ARS Horticultural Crops Research Laboratory in Fresno, California, he and colleagues James G. Leesch and Richard Gill have been testing carbonyl sulfide to control pests in stored products.

"This compound was effective against five species of insects that attack stored commodities," Zettler says. "We think it has potential as a replacement fumigant of dried fruits and nuts."

The compound, he says, is a colorless, odorless, tasteless gas similar to carbon disulfide and carbon dioxide. Although it has been known since 1867, carbonyl sulfide was just recently patented by the Australians to control insects and mites in postharvest commodities.

"Carbonyl sulfide is environmentally friendly, has good commodity penetra-

tion and aeration qualities, and can be toxic in a short exposure or at a reduced dose for a longer period. Also, it doesn't harm seed germination," Zettler reports.

Although the compound is patented as a grain fumigant, Zettler and colleagues have shown that it may be effective in fumigating other commodities as well. It is still experimental, and is not yet used in the United States since it has not been registered by the U.S. Environmental Protection Agency.

The five species of insects that succumbed to carbonyl sulfide in laboratory tests include: the confused flour beetle (*Tribolium confusum*), cigarette beetle (*Lasioderma serricorne*), sawtooth grain beetle (*Oryzaephilus surinamensis*), dried fruit beetle (*Carpophilus hemipterus*), and the navel orangeworm (*Amyelois transitella*).

Life stage susceptibility varied for the confused flour beetle—the most tolerant (hardest to kill) species—with the egg and pupal stages being most difficult to kill, requiring a larger dose of the chemical over a 24-hour period.

"Our research showed that toxicity of carbonyl sulfide is not always immediate in some insects," Zettler explains. "Since time required to kill the pest depends on dose, higher doses than we used may likely kill the pests more quickly."

On the downside, Zettler says that although carbonyl sulfide is a relatively stable molecule, under some conditions it can undergo a variety of reactions that could negatively affect commodities.

Zettler and colleagues at Fresno plan further studies on the phytotoxicity of this chemical and its effects on insect pests to fully assess its viability as a replacement fumigant of dried fruits and nuts.

# Recapturing Methyl Bromide Emissions

One way to help solve an important part of the methyl bromide emissions problem is to recapture, in an environmentally acceptable way, the chemical that escapes into the air from commodity and quarantine fumigations. Several groups in the United States and abroad are working on ways to effectively and efficiently recapture methyl bromide. Under a Cooperative Research and Development Agreement, James Leesch, ARS research entomologist, is working with GFK Consulting, Ltd., of San Clement, California, on one such approach to capture the methyl bromide and reuse its bromine content as a raw material.

"With our process, methyl bromide could be used for commodity and quarantine fumigations without damaging the stratospheric ozone layer," Leesch says. "If packinghouse, exporters, importers, and other commodity fumigators were to use this recapture technique, methyl bromide emissions could be reduced by as much as 95 percent." He is with the ARS Horticultural Crops Research Laboratory in Fresno, California.

Leesch says the process has some obvious pluses: It minimally affects the environment and does not alter established fumigation procedures.

Leesch and Gary Knapp of GFK Consulting trap the methyl bromide with activated carbon.

"We're essentially talking about putting a gas mask on fumigation chambers to prevent the release of methyl bromide to the atmosphere," Leesch says.

Instead of venting the gases from the fumigation enclosure directly into the atmosphere, as is done now, they plan to pass the air containing the methyl bromide through a transportable container filled with activated carbon. This activated carbon will trap 95 percent of the methyl bromide. Once the activated carbon has reached its adsorption capacity, it will be shipped to a central location where the carbon will be regenerated by flushing it with hot air or steam. The flushing removes the methyl bromide, which is thermally, or catalytically, converted to hydrogen bromide (HBr), carbon dioxide, and water. Then the HBr, either as it is or after chemical conversion to bromine, will be reused as a raw material. The regenerated carbon and its container are returned to another location, ready for further recapture of methyl bromide.

Advantages of this methyl bromide recapture process include the following:

- 1. It does not affect the treated commodity or the fumigation process. There will be virtually no change in fumigation procedures and 100 percent virgin methyl bromide will always be used. Protocol will be maintained with no change in methyl bromide concentration, fumigation time, temperature, or relative humidity.
- 2. It can be used at many locations with minimal impact on cost. The only equipment needed at each location is the ducting, the blower, and the controls to connect the fumigation enclosure to the transportable carbon container. Bromine recovery and carbon regeneration will be done at a single location, regardless of the number of fumigation locations.

# Recapturing Methyl Bromide Emissions—Continued

- 3. The spent carbon is not an RCRA (Research Conservation and Recovery Act) hazardous waste under 40 CFR 261. In fact, activated carbon is considered an excellent adsorbent for cleaning up and eliminating hazards, should methyl bromide be spilled accidentally.
- 4. Thermal recovery of bromine from byproducts or from waste is common practice in the bromine industry; waste is eliminated, and bromine is recovered. Methyl bromide flushed during regeneration of activated carbon is typical of waste that is already being treated.

In the first phase of their research project, Leesch and Knapp built and tested a bench-scale carbon adsorber to determine how methyl bromide concentration, type of carbon, temperature, and relative humidity affect adsorption capacity. They have done initial lab tests of the desorption process, and presented some of their results at the Methyl Bromide Conference in San Diego in November 1995. Leesch presented the work at the annual meeting of the Georgia Entomological Society, Savannah, Georgia, in March 1996 and will discuss it at the International Controlled Atmosphere and Fumigation Conference in Nicosia, Cyprus, in April 1996.

The current, second phase, focuses on repeated recapture of methyl bromide in the bench-scale column followed by regeneration with hot air.

"This will confirm the carbon's ability to adsorb methyl bromide and it will also show any decrease in adsorption capacity over time. Significant decreases in capacity require makeup carbon, which in turn adds costs to the overall process," Leesch says.

For the third, and final phase, Leesch and Knapp will build adsorbers to hold 150 pounds of carbon that, each minute, will treat 100 cubic feet of exhaust streams from commercial fumigation operations.

"These adsorbers will be big enough to warrant transporting them back to a prototype facility where the carbon can be regenerated and the bromine recovered," Knapp says. "And the bromine recovery for these experiments will be done in cooperation with the Great Lakes Chemical Company that has already provided part of the equipment needed for the study."

Knapp estimates the cost for a fumigator to use the overall process to be no more than about \$15 per pound of methyl bromide. This price, he says, would include delivery and removal of the activated carbon container and regeneration of the activated carbon. "The fumigator would need to supply the ducting, blower, and controls to connect his exhaust to the containers," he says.

Leesch and Knapp expect the final phase of the project to be completed some time this summer.

# Reducing Methyl Bromide Emissions

Scott Yates and colleagues from ARS and the University of California-Riverside have been exploring ways to decrease the amount of methyl bromide that escapes from fields into the atmosphere.

Yates, a soil scientist with the ARS-U.S. Salinity Laboratory at Riverside, and colleagues completed studies in 1993 and 1994 that measured methyl bromide emission from a field located at the University of California's Moreno Valley Field Station.

To reduce the amount of methyl bromide released into the air from fields, Yates and colleagues recommend that the chemical be applied relatively deep in organicsrich, moist soil under tarpaulins when temperatures are cool. Further packing the surface soil immediately after application and covering with high-barrier plastic should reduce emissions even more.

"Following current practices, we applied methyl bromide at a shallow depth and covered the field with a sheet of 1 millimeter polyethylene plastic," Yates reports. "About 61 percent of the methyl bromide we put on the field escaped into the atmosphere."

"In our second experiment, when methyl bromide was placed deeper in wetter soil and the daily temperatures were cooler, only 21 percent was lost."

Many soil-chemical processes affect the fate of any fumigant, including methyl bromide, Yates says. But an adequate balance of containment, degradation, and effective dosage must be maintained to lower emissions without sacrificing efficacy.

## Containment

"Perfect containment in the absence of degradation will not produce lower emissions unless the field remains covered indefinitely," he says. "Ideally, degradation will destroy methyl bromide in the soil before the plastic is removed but after achieving adequate pest control."

Since methyl bromide has a high vapor pressure, it moves through the soil easily. But injection depth, bulk density, water content, cracking of the soil, and the use of plastic all greatly affect how methyl bromide moves in the soil after application and how much is lost to the atmosphere.

Plastic films can reduce the amount of methyl bromide that escapes, Yates says, and new, impermeable materials are now available that can control containment even further.

He recommends that plastic be used rather than leaving the soil surface uncovered. "Recent experiments showed that, when injected at a shallow level, nearly all of the methyl bromide applied leaves the treated soil after a few days." Since the chemical stays in the soil much longer under lower permeability films, the application rate could be reduced without sacrificing efficacy. Reducing the rate translates into reduced emissions.

Yates' research showed that the depth at which methyl bromide is applied affects the amount that escapes into the atmosphere. Placing the compound at a greater depth can minimize its emission into the air during soil fumigation.

The studies also showed that disking and surface-packing closed the cracks in the soil above the injection sites. This, along with increasing the water content at the surface, helped reduce total methyl bromide emissions.

## **Degradation**

Degradation, or the breaking down, of methyl bromide in the soil keeps it from escaping into the atmosphere. Yates and colleagues found that less methyl bromide escaped from soils high in organic matter. Organic matter enhances degradation by providing a way for the chemical to uncouple. Once this occurs, the part of primary concern, bromine, remains in the soil as bromide. Therefore, increasing the organic matter in the soil allows less of the chemical to escape.

## **Effective Dosage**

If new ways to enhance methyl bromide's effectiveness could be developed, the quantity needed for agricultural uses would be reduced, thereby reducing the amount released into the atmosphere, Yates says.

In general, the amount and depth of injection depend on soil conditions and the type and distribution of target organisms. For strawberries, pests live fairly close to the soil surface because strawberries have shallow plant roots; but pests that attack grape roots are deeper in the soil. Therefore, the ideal injection depth for pest control differs for these two crops. For emission reduction, however, deep injection is preferred. For some conditions, like

coarse textured soils, good pest control can be obtained with deep placement of the chemical, and pest efficacy can be further increased with high-barrier plastics.

"We recently injected methyl bromide at 60 cm and covered the soil with polyethylene and high-barrier films to control citrus nematodes, *Rhizoctonia solani* fungi and yellow nutsedge seeds," Yates reports. "In soil covered with polyethylene, we got poor results from the methyl bromide, but we got good pest control in soil covered with high-barrier plastic."

To ensure sufficient levels of pest control from new emission-reduction technology, Yates and colleagues plan to test their ideas in different regions, soils, and environmental conditions.

# Controlled Atmospheres + Heat = A Methyl Bromide Replacement?

No one is sure that Joseph in Biblical times did not use controlled atmospheres to preserve the grain that kept starvation at bay during the 7 years of famine that followed the 7 years of plentiful harvests in Egypt. But it is a fact that, in ancient times, grain was stored in underground pits, which still exist in arid parts of the Middle East. Low oxygen levels in these pits kill pests, constituting a somewhat controlled atmosphere.

Although not quite that long ago, but for more than 30 years, ARS scientists have been studying the effects of controlled atmospheres on insect pests in stored grain. By modifying levels of oxygen, nitrogen, and carbon dioxide, they have been able to control these pests. Normal, or ambient, air composition is 78 percent nitrogen, 21 percent oxygen, and 0.033 percent carbon dioxide. Any significant deviation from this composition results in a modified, or controlled, atmosphere.

"As a result of 15 years of ARS research, in 1981 EPA approved controlled atmospheres as a means to manage insects infesting dried fruits and tree nuts," says Edwin Soderstrom, an ARS research entomologist. Soderstrom began his work on controlled atmospheres in the 1970's at the ARS Horticultural Crops Research Laboratory in Fresno, California. Research by scientists at ARS laboratories in Manhattan, Kansas and Savannah, Georgia, helped gain the EPA approval.

By adding or removing gases as needed, scientists have also developed modified atmosphere treatments that kill pests in fresh horticultural products. Although research using controlled atmospheres to manage insects on fresh produce has been ongoing for some time, there has been little commercial application of these treatments. Controlled atmospheres are successfully used in long-term storage of apples and several other fruits and vegetables. However, these treatments are not well tolerated by some horticultural commodities.

Some horticultural commodities, like cherries, must be free of insects of quarantine concern to the importing country. Japan, for instance, requires a methyl bromide treatment for fresh U.S. cherries entering Japan. This is to ensure that the codling moth (Cydia pomonella), a common pest of apples in Europe and North America, does not enter and become established in Japan.

"We shipped about 1.4 million boxes of sweet cherries to Japan in 1995, which is 27.3 percent of the total crop from California, Oregon, and Washington, the major U.S. cherry producing States," says Lisa G. Neven, a research entomologist at the ARS Yakima Agricultural Research Laboratory in Wapato, Washington. "Under current Japanese regulations, if acceptable alternatives are not developed, this market will be lost when methyl bromide is banned in 2001."

Neven has collaborated with Elizabeth J. Mitcham, a postharvest pomologist with the University of California at Davis, on an alternative treatment using controlled atmospheres and heat. "We combined controlled atmosphere with high temperatures and came up with a treatment that kills codling moth larvae in sweet cherries," Neven reports.

Temperature had been studied as a potential quarantine treatment for pests in temperate fruits, she says, and controlled atmospheres had been used for insect control in a few fresh commodities. However, it was not known if fruit could tolerate exposure to high temperatures under controlled atmospheres.

For their research to combine high temperatures with a controlled atmosphere, Neven and Mitcham designed unique quarantine chambers called CATTS (Controlled Atmosphere/Temperature Treatment System). These research chambers were built by Techni-Systems of Chelan, Washington, at the ARS Yakima lab and at the University of California-Davis. The unit controls temperature, humidity, and airspeed and differs from other hot-air treatment chambers in that it also controls atmospheric gases. Initial results with fruit were promising.

This past season, Neven cooperated with Steve Drake (ARS-Wenatchee, Washington). They subjected high-quality, fresh sweet cherries to 115°F to 117°F—with oxygen levels at 1.0 percent and carbon dioxide, 15 percent—for 60 and 25 minutes, respectively, without affecting the quality. Up to 2 weeks after treatment, there were still no undesirable changes in acidity, soluble solids, or firmness of the fruit.

"Our results show that using a combined treatment of a controlled atmosphere along with heat resulted in

more codling moth deaths than heat alone," Neven says. "Also, we found that the total length and intensity of a heat treatment can be dramatically reduced by using a controlled atmosphere."

Because this treatment is so different from methyl bromide, it is hard to make a comparison, but she says that it is in the ballpark for insect mortality levels required for a quarantine treatment. Neven plans to try the treatment on an industrial scale with scientists at Washington State University in the fall of 1996 to test its potential as a nonchemical quarantine treatment for sweet cherries that could replace methyl bromide.

# TECHNICAL REPORTS

Methyl Iodide as a Replacement for Methyl Bromide: Environmental Implications

**Principal Investigator**: S.R. Yates, U.S. Salinity Laboratory, Riverside, CA

Cooperators: J. Gan, F.F. Ernst, D. Wang, W.A. Jury, M.V. Yates, F. Gao, A. Mutziger, U.S. Salinity Laboratory and University of California, Riverside

Methyl iodide (MeI) has been recently proposed as an ideal replacement for methyl bromide in soil fumigation. Current research indicates that MeI is as effective as methyl bromide (MeBr) in controlling pests and is readily degraded in the lower atmosphere; hence should not significantly deplete stratospheric ozone. Since MeI is not a registered pesticide, however, there is virtually no information regarding its environmental behavior in agricultural soils. With the impending cancellation of MeBr and previous cancellation of other soil fumigants, it has become imperative to find and adopt methods for reducing emissions so that the remaining soil fumigants do not suffer a similar fate. Also, any decision to use alternative fumigants should be weighed in terms of the probable environmental consequences and the associated economic implications, and should be compared with methyl bromide.

There is a great need for more information on the soil-chemical parameters which characterize the fate

and transport of MeI. Since MeI has a similar chemical structure to MeBr, one would expect similar environmental behavior. Some information which is important in determining environmental fate and transport includes: atmospheric degradation, field-scale soil degradation, liquid-gas phase and liquid-solid phase partitioning, effective diffusion in soil and the various resistances to mass transfer between the soil and the atmosphere (e.g.volatilization). Other useful information on MeI which is generally available from chemical handbooks includes: water solubility (14,190mg/ L), log K<sub>ow</sub> (octanol-water coefficient, 1.69), molecular weight (141.9 g/ mole), vapor pressure (400 mmHg @ 25C), vapor density (4.89mg/mL) and boiling point (42.5 C).

We have recently started to obtain basic information on MeI transport. For example, although MeI and MeBr (1420 mmHg @ 20C) have very different vapor pressures, their Henry's Law constants are similar (K<sub>h</sub>,0.25 for MeBr and 0.22 for MeI at 25C). Henry's Law describes the equilibrium partitioning between the gas and liquid concentration and is an important measure of how readily a fumigant will diffuse through soils; since vapor diffusion is much greater than liquid diffusion. The free-air diffusion coefficients can be obtained using the Fuller-Schettler-Giddings correlation (Broadkey and Hershey, 1988) and is 6.96 cm<sup>2</sup>/min for MeBr and 6.28 cm<sup>2</sup>/min for MeI. Coupling these values to the gas-phase tortuosity gives the gas-diffusion coefficient for the soil.

Soil degradation is the transport parameter which is least known.

# **Technical Reports—Continued**

Recent experiments indicate that the degradation half-life for MeBr is approximately 10 days in a Greenfield sandy loam. Preliminary studies suggest that the MeI half-life is approximately 50 days in this soil. For a Linne clay loam soil with higher organic matter content, the half-lives were 5 and 10 days, respectively, for MeBr and MeI. A longer half-life for MeI would promote an increased residence time in soils. This may cause delays in planting, if the soil needs venting to reduce phytotoxicity, and would produce a greater total emission into the atmosphere compared to MeBr. Also, if irrigation follows fumigation, MeI's high water solubility and long residence time coupled to the reduced air-filled pore space after irrigation, will increase the probability of ground water contamination.

To demonstrate these ideas, a simulation of gas-phase diffusion in a sandy loam soil was conducted. The selected soil conditions are typical for fumigation and the model includes the effects of liquid-gas and liquid-solid partitioning, soil diffusion, degradation and volatilization at the surface through either a polyethylene or high-barrier plastic cover. The following soil properties were used for both MeBr and MeI: porosity 0.4cm<sup>3</sup>/ cm<sup>3</sup>, water content 0.15 cm<sup>3</sup>/ cm<sup>3</sup>, K<sub>d</sub> 0.2 cm<sup>3</sup>/g, bulk density 1.6g/cm<sup>3</sup> and mass applied 250 kg/ha at a depth of 25 cm. The Henry's Law constants were 0.25 (MeBr) and 0.22 (MeI); soil degradation half-lives were 10 days (MeBr) and 50 days (MeI); and the effective soildiffusion coefficients (e.g., D<sub>a</sub> =  $D_{\text{soil}}/R_{\alpha}$ ) were 0.376 (MeBr) and 0.301. (MeI). The resistance offered by the plastic material was obtained using Table 2 of Yates et al. (1996) which

reports the flux density of various fumigants through polyethylene and Hytibar (high-barrier) plastics. ForMeBr and MeI, respectively, the resistance offered by the high-barrier plastic is 75 and 148 times greater than with 1.4 mil polyethylene.

When 1.4 mil polyethylene plastic covers the soil, the model predicts that 43.5% of the applied MeBr and 67% of the applied MeI will volatilize. The peak flux densities were 0.10mg/cm<sup>2</sup>/ min for both MeBr and MeI. When a high-barrier plastic is used, the model predicts that only 1.4% and 1.9% of the applied MeBr and MeI escape from the soil. This suggests that the use of high-barrier plastics offers an important control mechanism for reducing emissions. Note that these estimates assume that the plastic remains on the field until soil gasphase concentrations are zero, which is considerably longer than the time period used in typical fumigations. Clearly, field experiments and simulations using more comprehensive models are necessary to refine these estimates.

The model predicts that MeI will move deeper into soils than MeBr and that using a high-barrier plastic will enhance downward movement. When the surface is covered with polyethylene, the model predicts that 2.0% and 0.2%, respectively, of the applied MeBr will move below 3m and 5m deep in soil. For MeI, 6.1% and 2.0% is predicted. When highbarrier plastic is used, the fraction of MeBr moving below 3m and 5m is slightly higher at 3.5% and 0.4%. For MeI, using a high-barrier plastic causes significant increases in deep movement: 17.9% passes 3m and 5.5% at 5m. This is due, principally,

to slower degradation and improved containment.

Although this gives a first glimpse into the behavior of MeI in soils, the effect of numerous model simplifications needs to be investigated before making any conclusions using the figures given above. Also, there is a great need for more information on the relevant environmental parameters for a wider range of soil and environmental conditions.

# Methyl Iodide: A Single Chemical Replacement for Methyl Bromide

James J. Sims, H.D. Ohr, N.M. Grech, Department of Plant Pathology; J. Ole Becker, Department of Nematology; M.E. McGriffen, Jr., Department of Botany and Plant Sciences, University of California, Riverside, CA 92521.

Methyl bromide is the most widely used and universally effective fumigant in the world. However, it has been subject to two major regulatory actions in the past few vears. The first was the United Nations' Montreal Protocol on Substances that Deplete the Ozone Layer which eliminates the use of methyl bromide in industrialized countries in 2010. Independently, the U.S. Clean Air Act will bring about a ban on production or importation in the USA after January 1, 2001. The reason for these actions is the current scientific opinion that methyl bromide emissions contribute significantly to the destruction of the ozone layer in the stratosphere.

We started this work about two years ago when we recalled that methyl iodide decomposes in light. This photolability of methyl iodide results in a very short residence time in the atmosphere of only a few days. This suggests that methyl iodide will not reach the stratosphere under normal circumstances and, therefore, will have an insignificant ozone depletion potential. The lifetime of methyl bromide in the atmosphere has been estimated to be 1.5-2 years.

Both methyl iodide and methyl bromide have well known chemistry being used as alkylating agents. Because of this similarity in reactivity, one would expect that methyl iodide would replace methyl bromide as a biocide. The literature shows very clearly that both compounds are considered toxic to animals. The documented chemical reactivity of both compounds is so similar that we expected that methyl iodide should act as a drop-in replacement for methyl bromide.

When we checked the biological literature for evidence of our conjecture, we found very little. Methyl iodide was tested as a potential fumigant of insects as long as 50 years ago and was shown to have good activity in a couple of subsequent studies. No literature appears to exist describing the use of methyl iodide in soil fumigation. It is known that the activity of many fumigants can be modified by their use in soil.

One further property of methyl iodide gives it an advantage over methyl bromide. Methyl iodide is a low boiling liquid with a boiling point of 42.5°C (108°F) while methyl bromide is a gas at ambient temperature and pressure. The ease of handling a liquid over a gas should increase worker safety.

Our testing of methyl iodide has been in soil against a broad range of organisms. Most of the tests have been done in comparison with methyl bromide (at the same molar concentration) and no treatment as controls. The organisms tested were: the fungi *Phytophthora citricola*, *P. Cinnamomi*, *P. parasitica* and *Rhizoctonia solani*; the nematode *Heterodera schachtii*; and the weeds *Abutilon theophrastii*, *Chenopodium album*, *C. murale*, *Convolvulus arvensis*, *Cyperus rotundus*, *Poa annua*, *Portulaca oleracea*, and *Sisymbrium irio*. In both

laboratory and field trials, when compared to equivalent molar rates, methyl iodide was equal to or better than methyl bromide in controlling the tested organisms.

Other environmental concerns are worth considering. Both chemicals have short half lives in water. Methyl bromide is hydrolyzed in 20 to 40 days and methyl iodide in 50 to 100 days.

Both are converted by this hydrolysis to methanol and, respectively, bromide ion or iodide ion. It has been estimated that methyl bromide has a half life of 14 days in the soil after a typical fumigation. This will be dependent on soil type and organic content. Some microbial consumption of methyl bromide in the soil has recently been reported. No such studies have been done for methyl iodide, but similar behavior would be expected. The fate of iodide in the environment is not well known, but unlike bromide, iodide is a recognized plant and human nutrient. The addition of iodide to salt is well known in this country. Lack of iodide is a major cause of mental illness in the world.

Based on its chemical, physical, and biological properties, methyl iodide is a logical candidate to replace methyl bromide.

## **Technical Reports—Continued**

# **Use of Hot Water for Nematode Control: A Research Summary**

Joseph W. Noling, nematologist, University of Florida, Institute of Food and Agricultural Sciences, Citrus Research and Education Center, Lake Alfred, FL 33850.

The use of hot water is not a new concept to nematode management. Belwey (1923) found that it took two million gallons of hot water per acre by a surface drench method to achieve nematode control. Compton (1936) devised a portable hot water sterilizer to be used at the end of a steam line for killing soil nematodes. Since the 1930's, most research has focused on procedural development of hot water dips for nematode disinfestation of plant materials. Only more recently have studies been reinitiated to evaluate soil applications of hot water for nematode control (Noling et al; 1994). This report attempts to summarize Florida research efforts on the use of hot water for nematode control utilizing a prototype hot water machine.

During the Fall of 1992, the first experiment with hot water was conducted and demonstrated that drip irrigation system delivery of hot water (104°F) could not provide effective nematode control, particularly at soil depths in excess of 8 inches. A second experiment in the spring of 1993 indicated that a "bottoms-up" approach, where a majority of total hot water soil input was delivered 16-18 inches below the finished plant bed, did not uniformly heat soil or provide nematode control within the surface 6 inches of soil. Since then, field experiments have focused on evaluating modifications to soil incorporation and hot water delivery systems. In some

studies, hot water was applied as a surface drench or injected into the soil directly at a depth of 8-10 inches via 10-12 steel chisels. Rototilling and rotovation soil incorporation methods have been evaluated. Tractor speeds were varied between 0.2 and 1.2 mph to examine the influence of dosage and total volume of hot water delivery per unit length of plant row. Water temperature and flow rates were held constant at temperatures between 220-230°F and 75-90 gpm. Soil temperatures were usually monitored at 3 or 4 depths, ranging between 2 and 18 inches, and compared with equivalent measurements in an untreated control.

The overall results from hot water experiments performed in Florida since 1994 indicate that irrespective of soil depth, maximum soil temperature elevations above that of the untreated control increase linearly with temperature treatment. The soil is generally heated very rapidly and in most cases. does not return to ambient conditions for many hours following treatment. The data also suggest that threshold levels of total hot water dosage required to elevate soil temperatures of a fine sandy soil (96% sand, <2% silt. clay, organic matter) to achieve nematode control under a plastic mulch covered plant bed is in the range of 30,000 to 70,000 gallons per treated acre. The wide range in water requirements is due to heating inefficiencies caused by differences in soil type and moisture content, as well as initial, seasonally defined, soil temperature conditions. For example, comparisons of field trials performed during the spring, summer, fall, and winter months showed that up to twice as much hot water may be required during the winter months when soil temperatures of 60°F occur. The method of soil incorporation also appears to be

very important in determining control. For example, rototiller mixing of soil in a vertical plane tends to increase heat losses by allowing cool air to intrude into the soil and allowing heated water vapor to escape with each revolution of the rototiller blade. But, rotovator incorporation, mixing hot water into soil in a horizontal plane, minimizes these losses by embedding the heated soil layer at the depth in which hot water is injected into soil. Other studies have also confirmed that irrigation water (79°F), introduced as simulated rainfall immediately after a hot water soil treatment, reduces maximum temperature development and increases the rate of heat loss, thereby reducing cumulative exposures of nematodes to elevated soil temperatures.

The depth at which lethal temperatures have been achieved (8-10 inches) also appears to be dependent upon soil incorporation depth. For example, in sandy soils, it is not possible to escape significant heat losses occurring via downward percolation of hot water into deeper, cooler nontarget soil profiles. In contrast, due to the slow downward percolation of water within heavier textured soils, water tends to pond at the depth of soil incorporation, and heat losses to deeper soil layers appear to be significantly reduced. Soil temperature gradients are immediate and transition zones between hot and cold soil narrow. To date, the most promising use of hot water soil treatments appears to occur in heavier textured soils or in soils where a compacted or impermeable layer restricts and delays downward, gravitational movement of hot water. The fear exists, however, that regardless of soil type, lack of pest control in soil horizons below the incorporation depth will allow subsequent pest recolonization and only delay pest impacts to crop growth.

New technological advances in hot water generation, delivery, distribution, and soil incorporation must still be developed to adapt hot water methods for broad scale, commercial field use. Further research is also needed to determine, in real time, hot water volume requirements for efficacious field soil treatment regimes. It also appears that commercial development and expanded use of hot water soil treatments for nematode control will also depend on overcoming other technical, environmental, and economic constraints. Because hot water alone is unlikely to substitute directly for methyl bromide soil fumigation, an integrated system of combining hot water with other approaches, must also be considered. These integrated approaches have not been intensively studied and additional research will be required to maximize pest-specific efficacy, consistency, and geographical adaptability.

# Methyl Bromide and Alternatives in Re-Registration Environmental Protection Agency Office of Pesticide Programs Washington, DC 20460

			Washington, DC 20460			
Chemical	Uses	New Use Registrations/ Applications	Re-registration Status	Special Review Status	Outstanding Data of Significance	Concerns
Methyl Bromide			Registration Eligibility Decision (RED) will not be scheduled until chronic toxicity studies are received and put into review. Earliest RED: late 1998.		—Chronic Toxicology Study in Rats due 11/30/97. —Mouse Heritability Locus Mutagenicity Assay due 12/31/97.	
Metam Sodium	Pre-plant soil fumigation-strawberries; fruits and nuts; vegetables; forestry, nursery, ornamentals; potting soil.		RED could be scheduled in late 1997 or early 1998.		—Turnip metabolism study is in review. Registrant seeks a waiver on other chemical residue studies.	—Recently classified as a Group B2 probable human carcinogen.  Known teratogen.  —Serious ground-water concerns/
Dazomet	Pre-plant soil fumigation-solanaceous crops; forestry, nursery, and ornamental crops; Also for soil treatment for nonbearing plants.	—4/25/91, approved use of dazomet before propagation or outplanting of nonbearing berry, vine, fruit, and nut crops. —2/28/96 Experimental Use permit(EUP) on strawberries, broccoli, tomatoes, and peppers granted.	Scheduled for late FY 1996 or early FY 1997.		Metabolism studies are being repeated.	Potential genotoxicity issues.

# Methyl Bromide and Alternatives in Re-Registration—Continued Environmental Protection Agency Office of Pesticide Programs Washington, DC 20460

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Chemical	Uses	New Use Registrations/ Applications	Re-registration Status	Special Review Status	Outstanding Data of Significance	Concerns
Telone (1,3-D)	Pre-plant soil fumigation—straw- berries; fruit trees and miscellaneous fruits and nuts; solanaceous crops; vegetables; forestry; single tree plantings; nursery, ornamental.		RED may be scheduled as early as FY 1997.	—Health concerns for workers and residents exposed to treated fields. —Registrant has agreed to incorporate label changes to mitigate risk by Aug. 1, 1996—EPA has determined that these measures will adequately reduce risks and, if they are followed, EPA will propose closing out the Special Review.		—Group B2 probable human carcinogen. —EPA will monitor groundwater study results and increased usage expected to occur as methyl bromide is phased out.
Chloropicrin	Pre-plant soil fumigation—strawberries; fruit trees and miscellaneous fruits and nuts; solanaceous crops; vegetables; forestry; nursery, ornamental; potting mix.		RED could be scheduled as early as FY 1997.		—Air monitoring studies are due in November 1996. —Oncogenicity Study in Rat is in review. —General metabolism study due April 1996.	—Preliminary study reports indicate potential concerns in areas of chronic toxicity in rats and oncogenicity in mice. —Potential applicator exposure and offsite movement of chloropicrin may be of concern.

# Methyl Bromide and Alternatives in Re-Registration—Continued Environmental Protection Agency Office of Pesticide Programs

	Concerns	—Organophosphate (neurotoxicity effects). —Group C possible human carcinogen. —Potential dietary, worker, and residential exposure	—Potential mutagenicity and neurotoxicity issues y —High acute 196. inhalation toxicity. ity 997.
Washington, DC 20460	Outstanding Data of Significance	Last data due March 1996.	—Chronic toxicity studies due October 1998. —Acute neurotoxicity study due August 1996 —90-day neurotoxicity study due August 1997
	Special Review Status	—Neurotoxicity and cancer concerns—9/28/95 EPA issued a Preliminary Determination to cancel all residential uses and uses on food stored in warehouses.  —11/93 final notice revoking tolerance for DDVP on packaged or bagged nonperishable processed food (effective date stayed indefinitely).	
	Re-registration Status	RED could be scheduled as early as 1997.	
	New Use Registrations/ Applications		RED could be scheduled by late 1999.
	Uses	Postharvest— nonperishable food stored in ware- houses.	Postharvest— fumigation of agri- cultural food and nonfood commodities, animal feeds, processed food commodities.
	Chemical	(dichlorvos)	Aluminum and Magnesium Phosphide

Source: U.S. Environmental Protection Agency.

# **Upcoming Meetings on Methyl Bromide**

## Washington, D.C.—October 21-23, 1996

The International Conference on Ozone Protection Technologies will be held again this year at the Washington Hilton & Towers, 1919 Connecticut Ave., NW, Washington, D.C., October 21-23. Formerly the International CFC and Halon Alternatives Conference, these meetings are sponsored by the Alliance for Responsible Atmospheric Policy, the U.S. Environmental Protection Agency, Environment Canada, and the United Nations Environment Programme.

Although meeting agendas have not been finalized, it is expected that methyl bromide will be discussed each day of the conference.

For information on registration and submission of papers, contact Heather Tardel, P.O. Box 236, 312 W. Patrick St., #2, Frederick, MD 21701; telephone (301) 695-3762, fax (301) 695-0175.

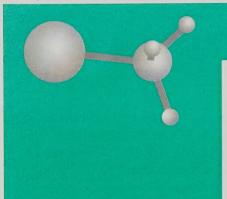
## Orlando, Florida-November 4-6, 1996

The third annual International Research Conference on Methyl Bromide Alternatives and Emissions Reduction is scheduled for November 4-6, 1996, at the Clarion Plaza Hotel, 9700 International Drive, Orlando, Florida. Again, the sponsors will be the U.S. Department of Agriculture, the Crop Protection Coalition, and the U.S. Environmental Protection Agency.

Objectives of the conference are to:

- Enhance scientific information and data exchange on methyl bromide alternatives research.
- Provide a forum for exchange of interdisciplinary scientific and agricultural information.
- Develop and distribute conference proceedings as a state-of-the-art methyl bromide alternatives source for researchers, users of methyl bromide, legislators, Government policy officials, and the general public.
- Support data gathering on potential alternatives to methyl bromide for future evaluation and prioritization.
- Monitor development of viable alternatives to methyl bromide.
- Evaluate technology transfer processes and incentive programs needed to implemen alternatives.

For additional information, contact Margie Upton, Methyl Bromide Alternatives Outreach, Fresno, California, phone (209) 244-4710, fax, (209) 224-2610.



Mention of trade names or commercial products in this publication is solely for the purpose of providing specific information and does not imply recommendation or endorsement by the U.S. Department of Agriculture.

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